The Use of Punched Cards in Molecular Structure Determinations. IV. Approximations to the Temperature Factor

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Citation: The Journal of Chemical Physics **19**, 511 (1951); doi: 10.1063/1.1748272
View online: http://dx.doi.org/10.1063/1.1748272
View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/19/4?ver=pdfcov
Published by the AIP Publishing

(1) The total heat capacity (translational, vibrational, internal, and external rotational) is calculated as usual, say at 100° increments.

(2) The enthalpy and entropy are calculated at the ice-point, 300°K, and 1500°K (or at any desired limit).

(3) The enthalpy and entropy at 100° increments above 300°K may then be calculated by numerically integrating the functions C_p^0 and C_p^0/T, respectively. The calculated values at the upper limit serve as a very close check.

This integration is easily carried out using lagrangian integration polynomials. The five-point polynomial seems the most applicable in this case, and it may be used to represent an integral:

$$\int_{T_0+mh}^{T_0+(m+1)h} f(T)dT = h\sum_{k=0}^{k=4} F_k(m)f(T_k),$$

where $m=0, 1, 2, 3$, and T_0 is the first of five consecutive temperatures, h is the increment, and values of $F_k(m)$ are given in Table I.[1]

TABLE I. Five-point lagrangian integration coefficients.

k	$m=0$	$m=1$	$m=2$	$m=3$
0	0.34861 11111	−0.02638 88889	0.01527 77778	−0.02638 88889
1	0.89722 22222	0.48055 55556	−0.10277 77778	0.14722 22222
2	−0.36666 66666	0.63333 33333	0.63333 33333	−0.36666 66666
3	0.14722 22222	−0.10277 77778	0.48055 55556	0.89722 22222
4	−0.02638 88889	0.01527 77778	−0.02638 88889	0.34861 11111

This calculation may be carried out quite rapidly on an ordinary calculator, and an error in calculation is almost always quite obvious. This method has been applied to several molecules, and in each case discrepancies between calculated and integrated results were traced to the calculated results, where smaller errors are not always so obvious. The time required for the calculation of thermodynamic functions of a molecule can be cut in half by the use of numerical integration as suggested here.

Tables of lagrangian interpolation coefficients are available,[1,2] and values at temperatures other than the even hundreds of degrees may be easily obtained (without making difference tables) by using these.

It is regrettable that so many of the scientists who calculate thermodynamic functions start at 298.16°K (25°C) rather than at 273.16°K, the ice-point, which serves as a basic reference point for relative enthalpy. The values at 25°C can be calculated readily, using an interpolation formula.[2]

[1] *Tables of Lagrangian Interpolation Coefficients*, Mathematical Tables Project of W. P. A. (Columbia University Press, New York, 1944), p. 390.
[2] Kobe and Pennington, Petroleum Refiner **30** (1951).

On the Polarization of Rayleigh Scattering as an Aid to Determine Molecular Configuration in Liquids*

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(Received February 19, 1951)

IT is well known that from the analysis of the vibration spectra (Raman and infrared absorption) much information can be obtained concerning the arrangement of the atoms in the molecule. In most cases, when these vibrational analyses are coupled with calculations of the entropy, satisfactory and unique solutions of the structure problem can be obtained. It is generally accepted that the determination of the state of polarization of the Raman lines is necessary for any rigorous vibrational analysis.

The purpose of this note is to point out the utility of a much older phenomenon, namely, the polarization of the Rayleigh scattering as an aid to solving the molecular structure problem.

It is well known that certain molecules in the liquid phase form associated complexes. In many cases this association is caused by hydrogen bonding. The phenomenon of association is accompanied, in general, by the observation of a boiling point very much higher than would normally be expected for liquids of the molecular weight in question.

Bhagavantam[1] has assembled a great deal of the data in the literature on the Rayleigh scattering of liquids. Inspection of Bhagavantam's table brings to light the following empirical regularities which qualitatively would be expected theoretically.

(1) Nonassociated liquids in which the molecular form approaches spherical symmetry show a high degree of polarization of Rayleigh scattering.

(2) Liquids which definitely are associated (the associated complex must certainly approach spherical symmetry) show a high degree of polarization of Rayleigh scattering.

(3) Nonassociated liquids, the molecular form of which is linear or approximately planar, produce highly depolarized Rayleigh scattering.

It should be noted further that, in general, the interaction of the light wave with the scattering entity to a large extent ignores the very light hydrogen atoms, e.g., liquid CCl_4 yields a $\rho=0.06$, while the chloroform molecule $CHCl_3$, which is also of tetrahedral structure, gives a $\rho=0.24$.

Recently, in this laboratory, the vibrational spectra of methyl hydrazine has been under investigation by Axford, Russell, and Janz. Considering only the heavy atoms, this molecule can be considered to be approximately linear. From various properties of liquid methyl hydrazine it might be supposed that association in the liquid state is present. The author suggested, from the above reasoning, that the Rayleigh scattering would be strongly polarized if association, which is presumably due to hydrogen bonding, was present. The experimental results obtained by Axford, Russell, and Janz, which will be published elsewhere, completely confirm the above contention.

In the case of liquids where association is unlikely, the state of polarization of Rayleigh scattering can be useful in deciding between different geometrical forms when the usual methods do not give a unique answer. This phenomenon might be particularly useful in the case of some of the boranes which exist as liquids, since the approximately planar, pyramidal, or "basket" structures should yield very different values for the polarization of the Rayleigh scattering.

* This research was carried out under Contract N6onr-269, Task V of the ONR.
[1] S. Bhagavantam, *Scattering of Light and the Raman Effect* (Chemical Publishing Company, New York, 1942), p. 84.

The Use of Punched Cards in Molecular Structure Determinations. IV. Approximations to the Temperature Factor

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THE punched-card method[1] which we use for the functions $\Sigma_i G_i \sin y_i x$ that have to be evaluated in the course of diffraction studies of the molecular structures of randomly oriented molecules requires that the coefficients G_i be constants, independent of x. However, in the expression for the intensity of diffraction, in our case,[2]

$$I(s)=\Sigma'_{i,j} Z_i Z_j r_{ij}^{-1} \exp(-a_{ij}s^2) \sin r_{ij}s, \qquad (1)$$

these coefficients often include the so-called temperature factor $\exp(-a_{ij}s^2)$, which takes into account the vibrational variation or an effective vibrational variation of the interatomic distance about its mean value r_{ij}. The quantity a_{ij} is $\frac{1}{2}\langle\delta r_{ij}^2\rangle_{Av}$ or, in order to make negligible the variation of some of the coefficients, an effective value $(\frac{1}{2}\langle\delta r_{ij}^2\rangle_{Av}-a_0)$.

Previously, this variation has ordinarily been approximated by constructing the corresponding distribution of the form $\exp\{-(r-r_{ij})^2(4a_{ij})^{-1}\}$ and approximating the required integration over the distribution by a sum of equally spaced $\sin rs$ terms having constant coefficients taken from this curve with suitable normalization. But in the absence of any readily applicable analysis of the situation, the desire for accuracy has usually led to the use of more terms than are actually necessary. Therefore, it was decided to work out to known accuracy several economized representations of this type for general application.

In order to simplify the work, the equal spacing of terms was retained. Then, in terms of appropriate reduced units, the amplitudes and spacings of terms were adjusted so that the approximation differs from the desired value by no more than a fixed maximum amount for $s \leqslant s_{\max}$, with $s_{\max}$ as large as possible. This has been done for 2, 3, 4, and 5 term representations and for maximum errors of $\pm 2\frac{1}{2}$, ± 5, and ± 10 percent of the ideal initial amplitude, and the results have been arranged in a table. For each of the twelve cases, this table gives directly the a values that can be achieved with spacings of integral hundredths of an A (somewhat unhappily, continuous variation of a is not afforded), the amplitudes of the terms of the representation, and the maximum values of a for which it is accurate, respectively, to $s=20$ and $s=30$; a simple interpolation gives the maximum a values for other values of $s_{\max}$.

Use of the table has simplified the punched-card summation of Eq. (1) by reducing by 50 percent, on the average, the number of terms used to represent temperature factors. It has also reduced to almost nothing the considerable preparatory work which was previously involved in setting up the calculations.

Copies of the table and notes on its use have been prepared and are available upon request.

* Contribution No. 1536.

[1] Shaffer, Schomaker, and Pauling, J. Chem. Phys. **14**, 659 (1946).
[2] R. Spurr and V. Schomaker, J. Am. Chem. Soc. **64**, 2693 (1942).

The Vibration-Rotation Bands of OH in the Photographic Infrared*

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RECENTLY, Meinel[1] has obtained in emission some of the vibration-rotation bands of the OH radical in the spectrum of the night sky. These bands lie in the region ~6800—~9000A and include the vibrational transitions (7—2), (8—3), (4—0), (9—4), (5—1), (6—2), and (7—3). Benedict, Plyler, and Humphreys[2] have found in emission from the outer cones of the oxy-acetylene and oxy-hydrogen flames numerous lines of the OH vibration-rotation bands (2—0), (3—1), and (4—2). We have recently also obtained the (4—0), (5—1), and (6—2) bands from the outer cone of the oxy-acetylene flame with a Baird 2-meter grating spectrograph at 8 A/mm using a 25μ slit and I-N plates hypersensitized according to the procedure described by Meinel.[1] Spectrograms of good contrast and density were obtained with exposure times of ~1½ hours under the conditions stated. In Fig. 1 is shown a densitometer tracing of a portion of the (4—0) and (5—1) bands. In the P-branch the spin doublets are well resolved as are the Λ-doublets for high K-values. The weaker background lines in Fig. 1 are the vibration-rotation lines of the H_2O molecule. At longer wavelengths, the H_2O lines become more intense. However, the P-branch lines in the (4—0) band, for example, are readily seen at least as far as $P(15)$. The OH bands in this spectral region can also be obtained from the outer cones of methane, ethylene, and hydrogen burning with oxygen. However, in these cases the OH lines are badly overlapped by the intense H_2O spectrum. Best results have been achieved with the oxy-acetylene flame obtained from an ordinary torch burning at stoichiometric proportions, when viewing the region of the outer cone closest to the tip of the reaction zone.

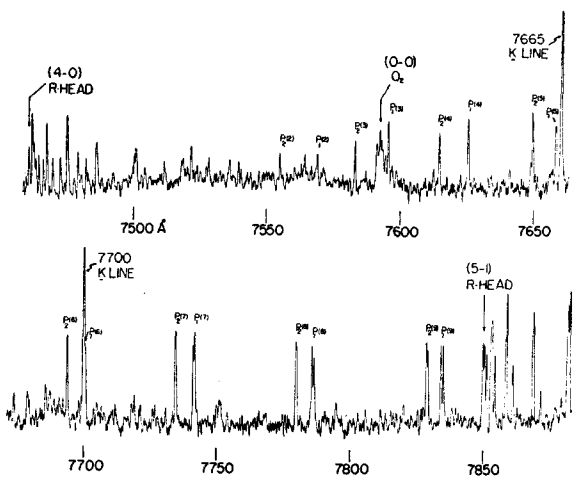

FIG. 1. Densitometer tracing of a portion of the (4—0) vibration-rotation band of OH. The R-branch heads of the (4—0) and (5—1) bands, the P lines of the (4—0) band, as well as the potassium resonance lines and the (0—0) band of the $^1\Sigma - {}^3\Sigma$ system of O_2, are indicated.

As yet, we have found no evidence in flame spectra of the vibration-rotation bands of OH reported by Meinel which originate from the higher vibration levels. Since the outer cone temperature of the oxy-acetylene flame is ~3000°K, this would lend support to Meinel's suggestion of resonance excitation of OH radicals in the night sky. As to be expected at the higher temperatures in the oxy-acetylene flame, the OH lines extend to higher K-values and the Q-branch is relatively weak as compared with Meinel's case.

Since the OH vibration-rotation bands discussed here can be obtained with high dispersion and resolution, an analysis of the bands and a determination of some of the molecular constants is in progress. We hope to report a complete account of this work in the near future.

* This work was supported by the U. S. Navy Bureau of Ordnance under Contract NOrd-7386.

[1] A. B. Meinel, Astrophys. J. **111**, 555 (1950); **112**, 120 (1950).
[2] Benedict, Plyler, and Humphreys, Bull. Am. Phys. Soc. **26**, No. 1, p. 50 (1951).

Comment on "Gas Bubbles in Solutions"

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IN a recent issue of this Journal, Epstein and Plesset[1] have derived formulas for growth and dissolving of gas bubbles in a liquid phase. Their treatment refers to a bubble at rest and is valid if transport of the dissolved gas takes place by diffusion only.

It seems interesting to consider the opposite limiting case, in which the mechanical motions in the system more than match the diffusion; for many applications (e.g., cavitation bubbles in a strongly turbulent medium or large bubbles of great buoyancy), this case is realized.

As Epstein and Plesset, I shall treat the growth of a single bubble in an infinite volume of fluid. Let us first investigate the influence of a strong translatory motion due to buoyancy. I shall use the notation of Epstein and Plesset except for letters, the meaning of which is specially explained. For laminar flow the velocity of the bubble is proportional to the square of the radius (reference 1, l.c.)

$$v \sim R^2. \tag{1}$$

Diffusion now comes into play for transport of the gas through the boundary layer only. Outside the boundary layer adhering to the bubble the motion of the fluid outweighs it, and we take c